ELECTROCOAGULATION AS A PRE - TREATMENT STAGE TO REVERSE OSMOSIS UNITS

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ABSTRACT

Reverse osmosis (RO) is used by coal seam gas (CSG) operators to treat produced water as it is a well-established and proven technology worldwide. Despite the suitability of RO, there are problems associated with RO technology such as membrane fouling which although not preventing use of RO does decrease effectiveness and increase operating costs. Hence, effective pre-treatment of water samples is essential. Electrocoagulation (EC) potentially can provide improved water purification compared to conventional coagulation prior to an RO unit. This paper provides the first reported study of EC for CSG water pre-treatment and compares the performance to a range of aluminium and iron based coagulants. It was found that EC was superior in terms of removal of silica, calcium, magnesium, barium and strontium in the produced water.

INTRODUCTION

Coal seam gas (CSG), also known as coal bed methane (CBM) is mostly comprised of methane (CH_4) and has become the subject of considerable commercial interest in recent years. Since the first production of CSG at Moura in Queensland by BHP, both the proved and probable (2P) reserves and production of CSG have increased almost exponentially.(Nghiem et al., 2011) The majority of CSG resources in Australia are found in the Bowen and Surat Basins in Queensland and in the Gunnedah, Gloucester and Sydney Basins in NSW and in the Clarence-Moreton basin on the NSW-Queensland border. The large volume of produced water associated with the production of CSG presents a challenge to industry. The CSG water mainly contains sodium chloride (ranging from 200 to 10,000 milligrams per litre), sodium bicarbonate and other trace elements. Reverse osmosis (RO) and ion exchange (IX) are the main technologies deployed for the treatment of CSG water, albeit RO dominates both in the number and treatment capacity of all CSG treatment facilicites in Australia. Pre-treatment of water is essential prior to the RO stage in order to control and prevent membrane fouling. Conventional pretreatment typically involves a coagulation, flocculation and particle separation operation. Dissolved air flotation (DAF) and microsand ballasted flocculation are the most commonly used particle separation processes in the CSG industry.

The search for reliable and cost-effective water treatment processes has spurred renewed interest in electrocoagulation (EC).(Holt et al., 2002) EC delivers the coagulants *in situ*, as the sacrificial anodes corrode when an applied potential is introduced, while hydrogen is evolved at the cathode to allow contaminant removal by flotation. EC provides an alternative to conventional chemcial dosing, where an inorganic metal salt such as aluminium chlorohydrate (ACH), polyaluminium chloride (PAC), alum, ferric chloride or ferric sulphate is added as primary coagulants and settling provides the path for pollutant removal.(Bratby, 2006) Literature suggests that EC is a promising technology for the removal of silica, suspended particulates, and hardness in water.(Malakootian and Yousefi, 2009) Hence, the main objective of this study is to examine EC applicability for the treatment of CSG water and compare the performance of EC with conventional chemical dosing in terms of the removal efficiency of suspended particulates, colloidal silica and various dissolved ions.

EXPERIMENTAL

The electrocoagulation (EC) cell used in the experiments was custom made by Ellers Water in Australia [Figure 1]. The EC reactor was connected to a DC power supply with polarity reversal function. A peristatic pump was used to deliver feed water into the EC reactor at a set flow rate which typically resulted in a contact time of 30 sec for each standard treatment. The EC reactor held 13 electrode plates with a net spacing between each plate of 3 mm. The EC cell had a vertical flow configuration with feedwater entering from the bottom and exiting at the top. A bi-polar electrode configuration was used with parallel connection. The EC experiments were carried out using both steel and aluminium plates. The first series of experiments involved treating CSG water with steel plates at 37.9, 28.4, 18.9 and 9.5 V for 30

and 60 s contact times. The second series of experiments followed the same protocol as outlined above with aluminium plates. After each experiment, the treated samples were agitated to break the microbubbles in order to aid settling in a 2 L measuring cylinder. Once the flocs settled, a small sample of the subnatant solution was removed for analysis.

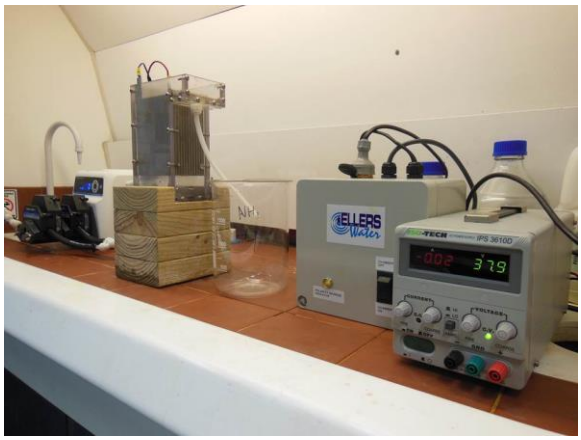

Figure 1: Bench scale electrocoagulation unit with a peristaltic pump, and DC power supply

The chemical coagulation experiments on the CSG water were carried out using a Platypus Jar Tester (Aquagenics, Sydney) with aluminium chlorohydrate (ACH) (Hardman Chemicals), polyaluminium chloride (PAC) (Omega Chemicals), aluminium sulphate (alum) (laboratory synthesis, see below), ferric chloride (Omega Chemicals) and ferric sulphate (Omega Chemicals) as chemical coagulants [Figure 2]. Aqueous aluminium sulphate was prepared from AR grade aluminium sulphate 18-hydrate granular material. The jar testing experiments consisted of 2 minutes rapid mixing at 190 rpm (equivalent to a G value of 500 s^{-1}), 10 minutes slow mixing at 50 rpm (equivalent to a G value of 75 s^{-1}) and a 30 minutes settling period. After settling for 30 minutes, subnatants were collected for analytical determination of residual ions in solution.

A PerkinElmer Optima 8300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used to analyse dissolved ions in the CSG water before and after treatment. Prior to analysis, all samples were adjusted to pH 2 by addition of 100 µL of 70% nitric acid which was first distilled using a Savillex DST-1000 unit. Images of flocs were taken using a Leica M125 light microscope.

X-Ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Co Ka radiation (1.7902 Å). Patterns were collected in the range 3 to 90° 2θ with a step size of 0.02° and a rate of 30s per step. Samples were prepared as a compressed powder in an aluminium holder.

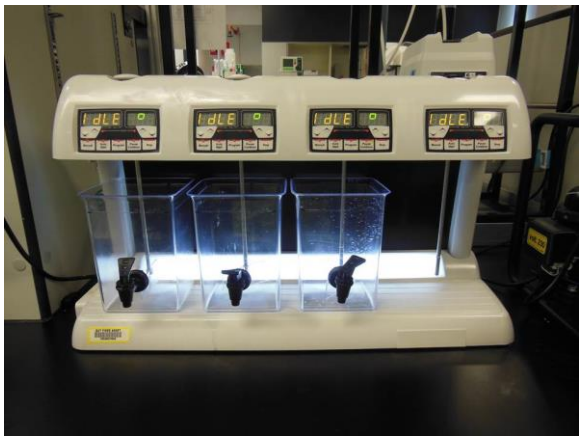

Figure 2. Platypus Jar tester comes with 2 L Jars

Infrared spectra were obtained using a 5700 Nicolet Diamond Fourier Transform Infrared spectrometer with a smart endurance single bounce diamond ATR (attenuated total reflectance) cell. Spectra over the 4000 - 350 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 m/s.

The coal seam gas water was supplied from the Surat basin by a major CSG producer. The precise composition of the CSG water is confidential.

RESULTS AND DISCUSSION

The parameters studied in the EC experiments included electrode material composition, voltage, current density and contact time. For the sake of brevity, this paper only shows the optimal performance recorded which was typically at a voltage of 37.9 V and a contact time of 60 s. More detailed evaluation of the experimental results will be published elsewhere. Similarly, for coagulation studies a range of concentrations were dosed in the CSG water samples. However, again for clarity of discussion we have only shown the best result for each coagulant and will report the fine details in separate publications.

Electrocoagulation (EC) Compared to Chemical Coagulation (CC)

In general, the experimental data revealed that for electrocoagulation aluminium electrodes were more efficient than steel electrodes in removing contaminants from the CSG water [Figures 3 to 8]. As indicated above, application of 37.9 volts produced the best performance in each case; indeed use of 9.5 volts potential to the solution did not generate any floc. Contact time also proved to be an important parameter in the treatment of CSG water by EC. The contact time

of 60s produced a better contaminant removal rate than 30s contact time. The results obtained from this study suggest that EC is a far superior technology than conventional chemical coagulation as discussed below.

In terms of the removal of calcium from the CSG water, electrocoagulation produced better results than conventional chemical coagulation in every case. EC with aluminium electrodes was able to remove all of the calcium ions from solution (100%), followed by EC with stainless steel electrodes (63%) [Figure 3]. In chemical coagulation, ACH had the highest removal rate of calcium (48%), followed by alum (37.5%), ferric chloride (36.8%), ferric sulphate (28.2%) and PAC (23%). The results obtained show that EC is almost twice as efficient as the conventional chemical coagulation with regards to calcium removal from the CSG water.

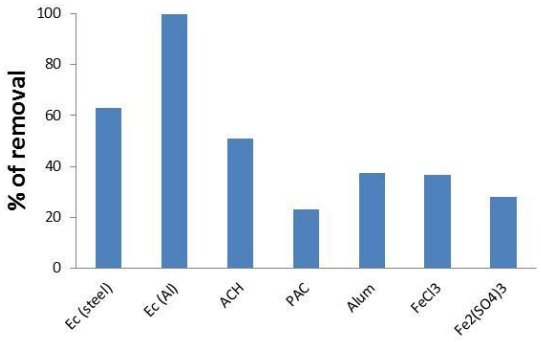

Figure 3 Comparison of the efficiency of EC with CC in the removal of calcium ions from CSG water

In terms of the removal of magnesium from CSG water, experimental results also showed that EC performs better than chemical coagulation. The highest magnesium removal was achieved by EC with aluminium electrodes (87%), followed by EC with stainless steel electrodes (77%). In comparison, the removal rates observed by chemical coagulation were significantly less, with ACH only extracting 28% of magnesium, followed by alum with 20.6% and ferric chloride 10.3% removal. PAC had less than 10% removal while ferric sulphate achieved no removal at all [Figure 4].

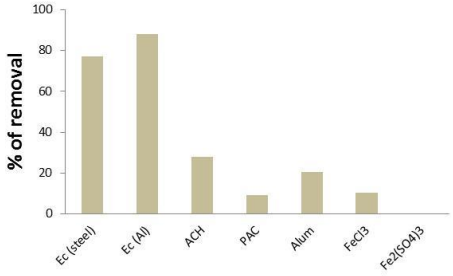

Figure 4 Comparison of the removal efficiency of magnesium from CSG water by EC and CC

Strontium was completely removed from the CSG water by EC with aluminium electrodes. In comparison, EC with stainless steel electrodes only managed to remove 78% of strontium. However, EC with stainless steel electrodes is still much more efficient than chemical coagulation in removing strontium from CSG water [Figure 5]. ACH, alum, ferric chloride and ferric sulphate all achieved a removal rate of approximately 40%. PAC is the least effective coagulant out of the five tested in strontium removal.

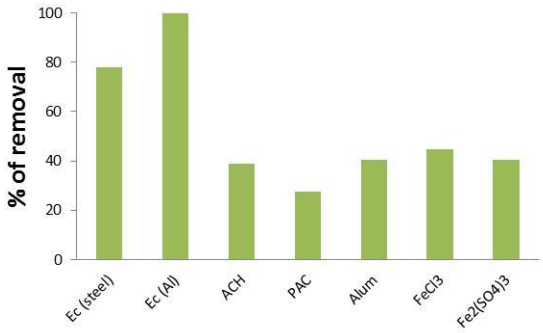

Figure 5 Comparison of the removal efficiency of strontium by EC and CC in the CSG water

In the study compiled by Murthy, 93% removal of strontium had been achieved using stainless steel electrodes and these materials proved to be better than aluminium electrodes (77% Sr(II) removal). Notably, the test parameters used in this latter EC experiment were quite different from those in this study: 50 minutes of contact time, current density of 8mA/cm^2, pH 5 and distance between electrodes 6 cm (Murthy and Parmar, 2011).

Barium was removed completely from the CSG water by EC with either aluminium electrodes or stainless steel electrodes [Figure 6]. Chemical coagulation did not achieve as high removal of barium as EC with ferric chloride getting 77% removal, followed by alum and ferric sulphate 72%. PAC and ACH exhibited the least barium removal, 62 and 66% respectively.

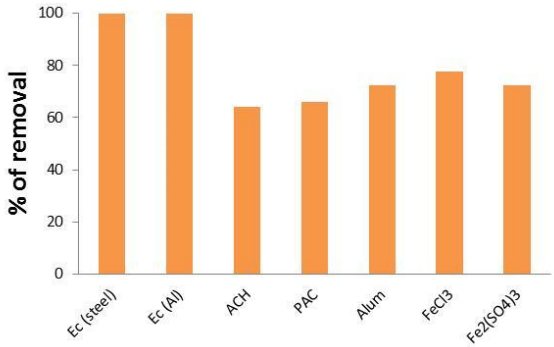

Figure 6 Comparison of the removal efficiency of barium by EC and CC in the CSG water

The results outlined above are in harmony with other reported studies using the electrocoagulation technique. For example, Malakootian used aluminium-rod electrodes to remove 95.6% water hardness using EC with test parameters 20 volts, contact time of 60 minutes and pH 10.1.(Malakootian and Yousefi, 2009) Similarly, Daneshvar *et al*. (Daneshvar et al., 2002) reported 94% removal of total hardness from brackish water using DC-electrocoagulation with iron electrodes and aeration as a means of water pre-treatment. The parameters they used in the experiment included current density of 22A/m^2, distance between electrodes 1.5 cm, contact time of 10 minutes. Notably, in this study the EC treatment time was substantially reduced compared to published studies, suggesting the EC design used was potentially superior.

The highest silica removal from the CSG water was achieved by EC with aluminium electrodes (98% removal), followed by EC with stainless steel electrodes (84% removal). The results obtained from EC showed better performance in silica removal from the CSG water than chemical coagulation [Figure 7]. PAC had the highest silica removal from the CSG water (59.4%), followed by ACH (50% removal) and Alum (40.2% removal). Ferric chloride and ferric sulphate had the lowest silica removal with only 21.8% and 10.6% respectively.

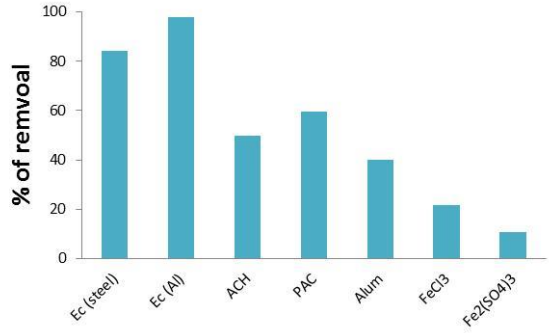

Figure 7 Comparison of removal efficiency of silica by EC and CC in the CSG water

Den and Wang (Den and Wang, 2008) reported 80% removal of silica from brackish water by electrocoagulation with bipolar aluminium electrodes under a current of 0.5 A and contact time of 30 minutes. They also concluded that the bipolar electrode configuration was more efficient than the monopolar configuration in regards to silica removal.

Boron was an element in the CSG water that was not removed effectively by both EC and chemical coagulation. Experimental results showed that EC with aluminium and stainless steel electrodes only managed to remove 12.9 % and 5.3% from the CSG water respectively. ACH was the only chemical coagulant able to exert a slight removal of boron (6.5%). These results were somewhat surprising in consideration of previously published data. For example, Yilmaz *et al.* (Yilmaz et al., 2008) reported 95% boron removal from geothermal waters by electrocoagulation with current density of 3 mA/cm^2, pH kept at 8 and 30 minutes contact time. In another study on the removal of boron from produced water by EC, Ezechi *et al.* (EZECHI et al.) reported that the highest boron removal occurs between pH 7 – 8. In their study, 96.7% boron removal from the produced water was obtained at pH 7.84, with a current density of 12.5 mA/cm^2 and interelectrode distance of 0.5 cm.

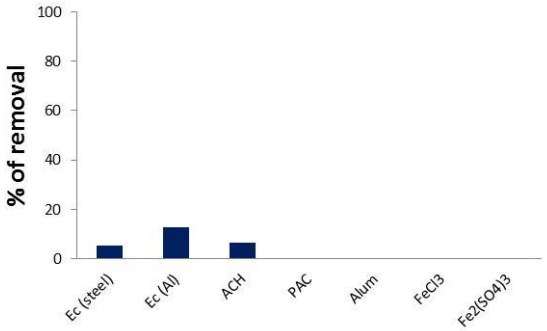

Figure 8 Comparison of the removal efficiency of boron by EC and CC

The precise reason for the low boron removal from CSG water is as yet not clear. The relatively high pH of the CSG water may be one explanation, or alternatively the boron chemistry in the CSG water may be more complicated compared to simple solutions of boric acid in pure water.

FT-IR analysis

The Infrared spectrum of the floc sample from electrocoagulation using stainless steel electrodes shows a broad band at 3370 cm^{-1} (not shown for sake of brevity) and 3 features in the region between 1200 cm^{-1} and 1700 cm^{-1} [Figure 9]. The broad band at *ca*. 3370 cm^{-1} indicates the presence of significant amounts of molecular water. Likewise, the band at 1635 cm^{-1} may partly be ascribed to the deformation mode of H_2O. The two bands at 1492 and 1352 cm^{-1} represent the C – O stretching modes of adsorbed carbonate species (Hausner et al., 2009). The band at 889 cm^{-1} in turn appeard due to the C – O total symmetric stretch of the carbonate species. (Hausner et al., 2009) The IR spectrum of the aluminium floc sample from EC also exhibits similar bands in the region of 1200 and 1700 cm^{-1} as the iron electrode sample with some variation in peak intensity noted. The spectra were comparable to those reported after carbon dioxide adsorption to the surface of aluminium oxyhydroxide and iron oxide.(Pierre-Louis et al., 2013)

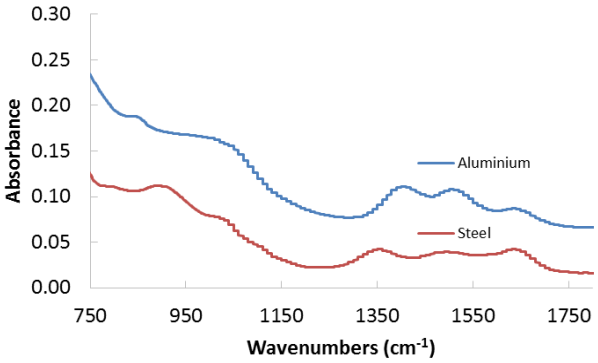

Figure 9 FT-IR spectra of aluminium and iron flocs generated by EC

The IR spectra of the flocs from ferric chloride and ferric sulphate have similar absorption bands. The three bands appearing in the region of 1200 and 1700 cm^{-1} correlate to carbonate adsorption on ferrihydrite. (Pierre-Louis et al., 2013) In the ferric sulphate sample, the bands were evident at 1630, 1514 and 1378 cm^{-1} whereas with ferric chloride, the peaks were present at 1635, 1520 and 1374 cm^{-1} [Figure 10].

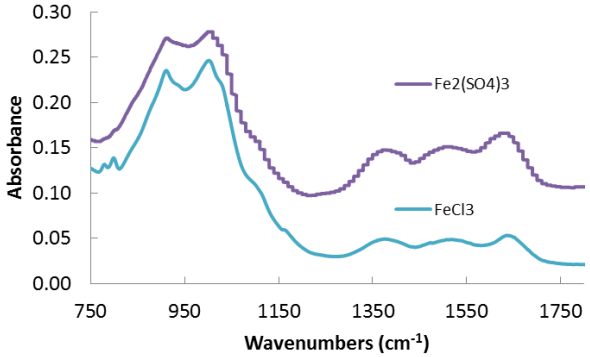

Figure 10 FT-IR spectra of flocs generated from ferric coagulants

The IR spectra of the aluminium flocs produced from ACH, PAC and alum all exhibited similar IR absorption bands. In the region between 1200 and 1700 cm^{-1}, ACH sample was characterized by vibrations at 1634, 1506 and 1412 cm^{-1}, PAC bands were 1632, 1519, 1414 cm^{-1} and alum peaks at 1635, 1520 and 1413 cm^{-1}. The above spectral evidence seems to suggest carbonate absorption on aluminium oxyhydroxide (Baltrusaitis et al., 2011). The FTIR spectra presented above suggest that the surface chemistry of the flocs is similar with a propensity for both aluminium and iron based systems to adsorb carbon dioxide when exposed to atmospheric conditions.

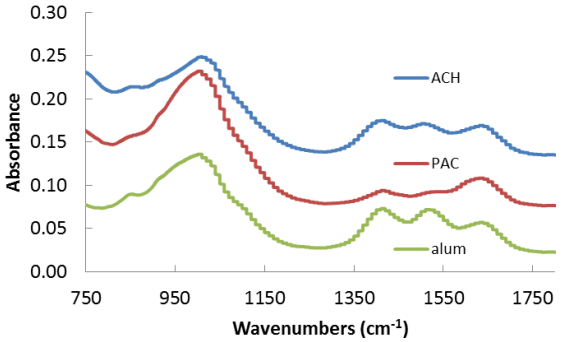

Figure 11 FT-IR spectra of flocs generated from aluminium coagulants

XRD ANALYSIS

The XRD diffraction patterns of the dried iron floc samples from EC indicated the presence of goethite (FeOOH) and possibly ferrihydrite. The diffraction pattern of the iron floc sample suggests that the sample has small domain sizes and probable amorphorous content. On the other hand, the diffraction pattern of the aluminium floc sample produced by EC suggests the presence of boehmite (AlOOH) [Figure 12]. The diffraction pattern of the dried floc samples obtained from aluminium coagulants such as ACH, PAC and alum does not suggest the presence of boehmite or any other forms of aluminium oxyhydroxide [Figure 13].

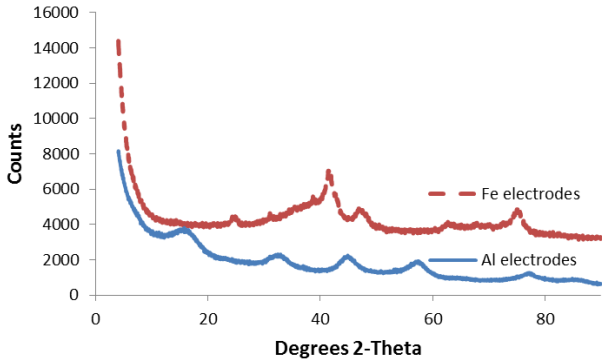

Figure 12 XRD diffraction patterns of dried flocs samples from EC

The weak diffraction patterns of the dried floc samples produced by aluminium coagulants suggest that the flocs produced by chemical coagulants are not as crystalline as the flocs produced by EC with aluminium electrodes. The diffraction patterns of the dried flocs produced by ferric coagulants is also weak and broad, suggesting a large proportion of the sample is amorphous. It is difficult to conclude the presence of goethite or any other kind of iron oxide in the sample.

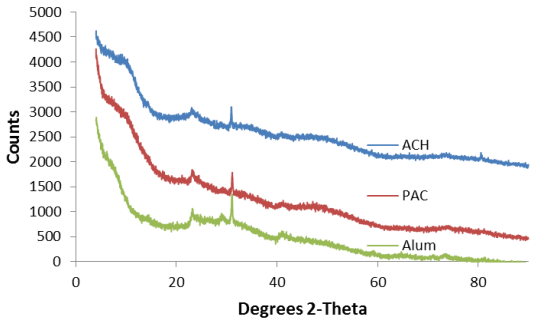

Figure 13 XRD diffraction patterns of dried floc samples from aluminium coagulants

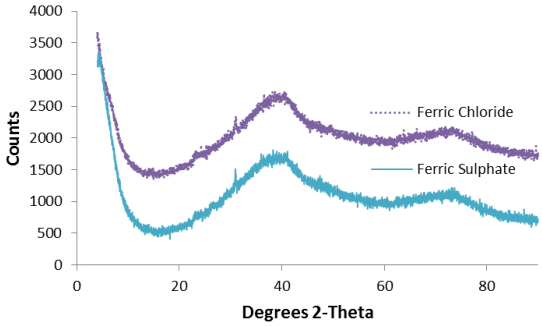

Figure 14 XRD diffraction patterns of dried floc samples from ferric coagulants

Qualitative image analysis

The flocs produced by electrocoagulation were examined with a light microscope. The colour and shape of the flocs generated by stainless electrodes appears to be quite different from the flocs generated by aluminium electrodes. The iron flocs were characterized by green and yellow colour [Figure 15], whereas aluminium flocs have a more greyish colour [Figure 16]. The ACH flocs appeared to be more dense and to possess a more sophisticated network [Figure 17]. This observation may tentatively explain why ACH produces the best removal of contaminants from the CSG water, in terms of the various coagulants used. The flocs generated by PAC [Figure 18] and alum [Figure 19] look somewhat similar. On the other hand, flocs produced from ferric sulphate [Figure 20] and ferric chloride [Figure 21] are notably different from the aluminium flocs. Even though the exact mechanism of the floc formation with each different type of coagulant is unknown, it seems that the size and density of the flocs play some role in the contaminant removal ability from CSG water.

Harif *et al*. (Harif et al., 2012) in their study of flocculation mechanisms and resulting floc characteristics, discovered that the flocs produced by EC have a negligible repulsive barrier, thus enabling accelerated growth. Hence the EC produced

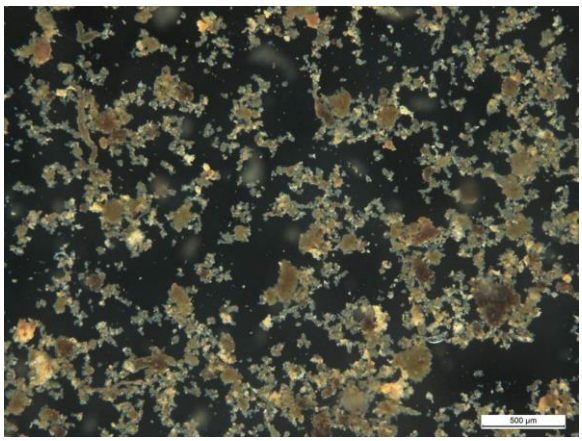

Figure 15 Light microscopy image of iron flocs produced by EC with 37.9 v and 60 sec of contact time (40 X)

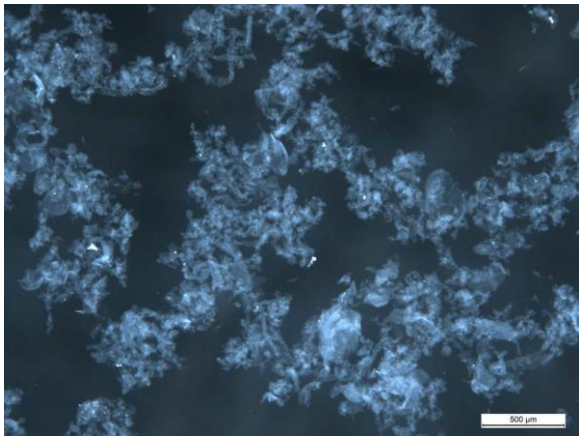

Figure 16 light microscopy image of aluminium flocs produced by EC with 37.9v and 60 sec of contact time (40 X)

flocs seem to be tenuous and are more susceptible to applied shear force, which results in floc restructuring leading to a more compact floc at the end of the process. On the other hand, flocs from chemical coagulation have a high repulsive barrier, leading to slower growth profile. As a result, more strong and compact flocs are produced which leads to structural evolution into a more porous structure. The flocs formed by chemical coagulation in this experiment are indeed more compact, well defined and denser than the flocs formed by applied current, which look more open and transparent.

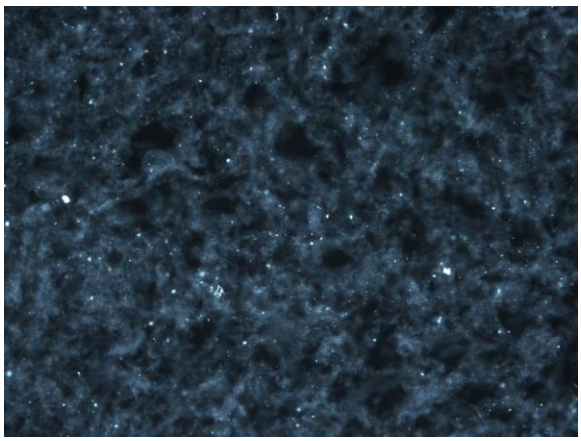

Figure 17 Light microscopy image of ACH flocs at 50 X

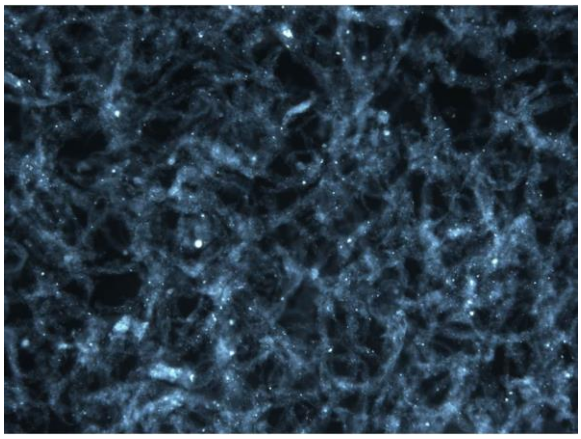

Figure 18 Light microscopy image of PAC flocs at 50 X

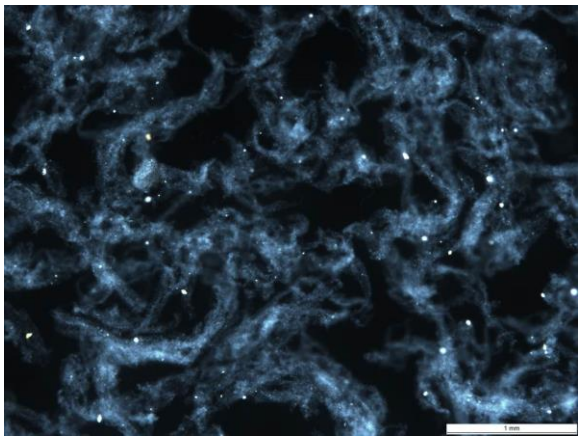

Figure 19 Light microscopy image of alum flocs

CONCLUSION

Results obtained in this study have shown that electrocoagulation is a superior technology compared to conventional chemical coagulation in the removal of water hardness and silica from CSG produced water.

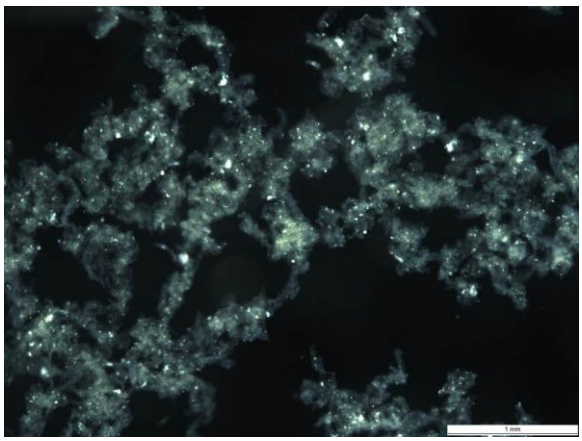

Figure 20 Light microscope image of Ferric sulphate flocs at 50 X

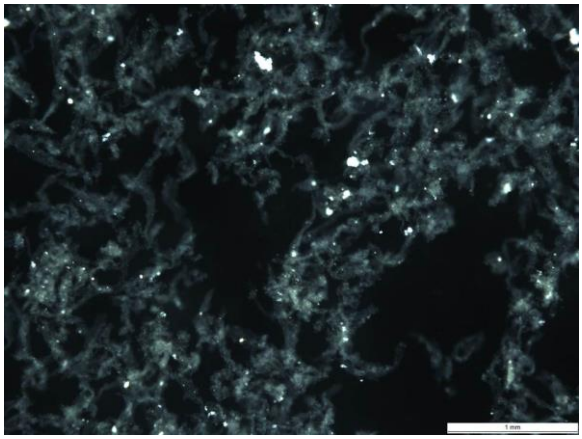

Figure 21 Light microscope image of ferric chloride flocs at 50 X

In this experiment, EC was able to achieve a 100% removal of calcium, strontium and barium, 98% silica and 87% magnesium from the CSG water. The parameters used to achieve this removal were a potential of 37.9 V and 60 sec of contact time, with aluminium electrodes. Even though stainless steel electrodes did not produce the same removal rate as aluminium electrodes, they still outperformed all of the chemical coagulants tested in this experiment.

Future studies will be directed at understanding the performance of electrocoagulation with a wider range of coal seam gas water samples. It is expected that the variation in total dissolved solids content may influence electrocoagulation operation in that higher salt concentrations are more conductive (thus potentially enabling cost reductions due to reduced voltage requirements). Power consumption will also be calculated once a deeper understanding of the treatment process using electrocoagulation is gained. As indicated above, coal seam gas water composition is anticipated to influence the performance of electrocoagulation, thus economics must be presented in terms of not one single number but as a function of the variables involved.

ACKNOWLEDGMENT

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